



Photo-assisted catalytic methanation of CO in H₂-rich stream over Ru/TiO₂



Xiahui Lin^{a,b}, Kai Yang^a, Ruiru Si^a, Xun Chen^a, Wenxin Dai^{a,*}, Xianzhi Fu^a

^a Research Institute of Photocatalysis, Fujian Provincial Key Laboratory of Photocatalysis—State Key Laboratory Breeding Base, Fuzhou University, Fuzhou 350002, China

^b College of Chemistry & Material Science, Longyan University, Longyan 364012, China

ARTICLE INFO

Article history:

Received 23 June 2013

Received in revised form

15 September 2013

Accepted 22 September 2013

Available online 29 September 2013

Keywords:

Methanation of CO

Ru/TiO₂

Photo-assisted effect

Electron transfer

ABSTRACT

Ultraviolet (UV) light was introduced into the process of hydrogenation of CO over Ru/TiO₂ catalyst which were prepared by a facile impregnation–reduction method. It is found that UV irradiation can promote the conversion of CO into CH₄ over Ru/TiO₂ at 150–220 °C. Based on the testing results of XPS, FT-IR and TPSR for Ru/TiO₂ under UV irradiation, it is proposed that the photo-generated electrons induced by the band-gap excitation of TiO₂ can transfer to Ru along with the increase of surface electron density of Ru sites. This will further promote the adsorption of CO and its activation at Ru sites, resulting in the photo-enhancement of the methanation of CO.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The potential application of hydrogen as a future global energy carrier has stimulated enormous interests in the research of hydrogen generation and purification technology, especially in the study of the proton exchange membrane fuel cells (PEMFCs) due to their high energy conversion efficiency and zero or nearly zero emissions [1,2]. However, the H₂ stream produced by reforming CH₃OH or other alcohols needs to be purified to reduce the concentration of CO to the extremely low levels (<50 ppm), as dictated by the poisoning limit of PEMFC electrodes [3–8].

Methanation of CO over various supported metal catalysts (CO(g) + 3H₂(g) → CH₄(g) + H₂O(g), ΔH° = −205.8 kJ mol^{−1}), as a promising alternative to remove the residual CO in H₂-rich stream for PEMFC application, has been widely investigated [9–16] due to its following advantages: (1) The reaction can conduct without any additional reactant required; (2) the product of CH₄ can act as an inert diluent in the fuel cell and be used as the fuel to heat the steam reformer; (3) The amount of H₂ consumed during the reaction process is negligible due to the low content of CO. However, the reaction temperature of CO methanation is relatively high, which maybe benefit to the occurrence of the reverse water–gas shift

reaction. Moreover, the reaction temperature range of exhibiting high conversion of CO is very narrow. Therefore, how to improve the low-temperature activity and stability of the reaction system has attracted much attention.

Although the reaction mechanism of CO methanation over the oxide-supported metal catalyst (such as Ni, Ru, Rh etc.) is still not fully known, it is widely accepted that the methanation of CO is mainly dependent on the adsorption of CO and its activation at active metal sites [13–16]. Since a high electron density of metal nanoparticles is beneficial to the adsorption of CO and its activation at metal surface [17–19], our work group has ever introduced ultraviolet (UV) light into the process of oxidizing CO over Au/TiO₂ catalyst and found that UV irradiation could promote the oxidation of CO [20,21]. We also found that this phenomenon could also occur on the oxidation of CO over Pt/TiO₂ catalyst under UV irradiation [22]. Moreover, we suggested that the promoted effect of UV light could be attributed to the increase of surface electron density of Au or Pt sites induced by photo-generated electrons transferring from TiO₂ to Au or Pt. This will further promote the adsorption of CO and its activation at Au or Pt sites.

Based on the above study, in this paper we have introduced UV light into the reaction system of CO methanation over a TiO₂ supported Ru catalyst (Ru/TiO₂). It is expected that UV light can promote the increase of surface electron density of Ru sites and then the adsorption of CO and its activation at Ru sites, which benefits to the methanation of CO over Ru/TiO₂. Fortunately, it is found that the reaction activity of CO methanation does be greatly enhanced

* Corresponding author. Tel.: +86 591 83779083; fax: +86 591 83738608.

E-mail addresses: daiwenxin@fzu.edu.cn (W. Dai), xzfu@fzu.edu.cn, daiwenxin@fzu.edu.cn (X. Fu).

under UV irradiation. Furthermore, a mechanism of photo-assisted catalytic methanation of CO over Ru/TiO₂ is proposed.

2. Experimental

2.1. Preparation of catalysts

Ru/TiO₂ catalyst was prepared by a facile impregnation–reduction method. First of all, a prepared TiO₂ sol [23] was dried at 80 °C and calcined at 450 °C for 3 h to prepare TiO₂ powder. Then, a 1.0 g as-prepared TiO₂ powder was immersed into a 1.0 mL of RuCl₃ solution (0.1 M, 1.0 g RuCl₃ dissolved in 50 mL 0.1 M HCl) for 12 h at room temperature before drying at 80 °C. This obtained powder was reduced with 50 mL of 0.1 M aqueous solution of NaBH₄ (mixed with 0.1 M NaOH) for 1 h and rinsed with deionized water to remove Cl[−], Na⁺ and other excess ions. After drying in a vacuum oven at 80 °C for 5 h, a Ru/TiO₂ sample containing 1.0 wt% Ru was obtained.

In addition, a γ -Al₂O₃ supported Ru catalysts (Ru/Al₂O₃, 1.0 wt% Ru) was prepared by the same procedures shown as above, except that a γ -Al₂O₃ powder instead of TiO₂ powder.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) investigation was carried out on a JEOL JEM-2010 EX with field emission gun a 200 kV. X-ray diffraction (XRD) pattern was recorded on a Bruker D8 Advance powder X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. The textual data of the samples were measured by N₂ adsorption at liquid N₂ temperature with a micromeritics ASAP 2020 BET analyzer. Before the analysis the sample was outgassed at 250 °C under vacuum for 4 h. The optical properties of the samples were characterized by a Cary 500 UV–Vis diffuse reflectance spectroscopy (DRS) with BaSO₄ as the internal reflectance standard. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific ESCALab250 spectrometer with a monochromatic Al K α as the X-ray source, a hemispherical analyzer, and sample stage with multiaxial adjustability to obtain the surface composition of the sample. All of the binding energies were calibrated by the C1s peak at 284.6 eV.

2.3. Catalytic performance

The methanation of CO was conducted in a fixed bed flow reactor under an atmospheric pressure. 600 mg catalyst with a grain size of 0.2–0.3 mm was packed in a flat-plate quartz cell (30 × 20 × 0.5 mm) which was heated by an electric resistance board. A K-type thermocouple was inserted into the reactor to monitor the temperature of the catalyst bed. The reactions were performed at the temperature range of 160–210 °C. To ensure that Ru species is reduced to the metallic Ru as much as possible, prior to introduce reaction stream, each catalyst was reduced at 300 °C for 1 h in the stream of 40 vol% H₂–He with a flow rate of 100 mL min^{−1}. During the photo-assisted reaction process, UV light (produced by a 300 W Xenon lamp with a UV-reflectance filter, 300 nm < λ < 420 nm) was introduced into the surface of quartz cell. For testing the activity of catalyst in dark, the quartz cell was enclosed with Al foils to cut off light irradiation. The feed stream was fed at a total flow rate of 100 mL min^{−1} with the following composition: 0.5 vol% CO, 20.0 vol% H₂ and a balance He. The effluent stream was analyzed using an online gas chromatograph (Agilent 4890D, TDX-01) system equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). GC analysis results displayed that CH₄ was the only product over Ru/TiO₂ under

Table 1

The textural data of TiO₂ and Ru/TiO₂ samples.

Sample	Specific surface area (m ² g ^{−1})	Pore volume (mL g ^{−1})	Pore diameter (nm)
TiO ₂	90.15	0.15	6.46
Ru/TiO ₂	92.36	0.17	7.12

UV irradiation or not, indicating that the selectivity of CO methanation over Ru/TiO₂ is 100% in the all cases. Therefore, the activity of catalyst was evaluated by the conversion of CO, which could be calculated on the basis of the content change of CO in the feed and effluent stream.

2.4. Chemisorption of CO

The chemisorptions of CO on samples were measured with an FT-IR spectra instrument (Nicolet Nexus, Model 670) containing a controlled environmental chamber equipped with two CaF₂ windows. A self-supporting sample pellet (20 mg) of sample was mounted on a holder in the chamber. This sample was pretreated in a vacuum at a pressure of 10^{−1} Pa at 150 °C for 2 h. After cooling to room temperature, the adsorbed gas was introduced into the sample. After 30 min, an absorption spectrum was obtained. For testing FT-IR under UV irradiation, a UV light (300 W Xenon lamp with a UV-reflectance filter) was introduced into the surface of sample during the process of adsorbing gas. All spectra were recorded by a DTGS KBr detector in the transmit mode.

2.5. Temperature programmed surface reaction (TPSR)

The activation of CO species adsorbed at the surface of catalysts was investigated by the temperature programmed surface reaction (TPSR) tested in Micromeritics Autochem 2910 instrument. Prior to the introduction of the adsorbed gas, a 100 mg of powder sample was firstly degassed in a high purity He stream (20 mL min^{−1}) at 120 °C for 30 min. After cooled down to room temperature, a specific process for the sample proceeded as follows: (1) Introducing CO (10 vol% CO–He) to be adsorbed for 30 min at room temperature with a flow rate of 20 mL min^{−1}. (2) Switching He stream for 30 min. (3) Heating to 500 °C at a ramping rate of 10 °C min^{−1} in a stream of 5.0 vol% H₂–Ar with a flow rate of 25 mL min^{−1}, and recording the mass spectrometry signals with m/e of 16 to detect the masses of CH₄. For testing TPSR under UV irradiation, a UV light (300 W Xenon lamp with a UV-reflectance filter) was introduced into the surface of sample during the process of adsorbing CO.

3. Results and discussion

3.1. Catalyst characterization

The TEM image of Ru/TiO₂ in Fig. 1a shows that single Ru particles with sizes of 5–10 nm are deposited on the surface of TiO₂ particles. Here, Ru nanoparticles mainly present a (1 0 1) surface plane (the width of the surface unit cell is 0.20 nm), and TiO₂ particles mainly present a typical (1 0 1) surface plane (the width of the surface unit cell is 0.35 nm) (seen in Fig. 1b).

The XRD patterns of TiO₂ and Ru/TiO₂ in Fig. 2 shows that TiO₂ presents the structure of a major anatase, a minor rutile and brookite in both TiO₂ and Ru/TiO₂. However, the characteristic diffraction peaks of Ru species are not observed in the XRD pattern of Ru/TiO₂. This indicates that the loaded Ru nanoparticles are highly dispersed at the surface of TiO₂. Moreover, Ru/TiO₂ exhibits a textual property (pore radius, pore volume and specific surface area) similar to that of pure TiO₂ powder (seen in Table 1).

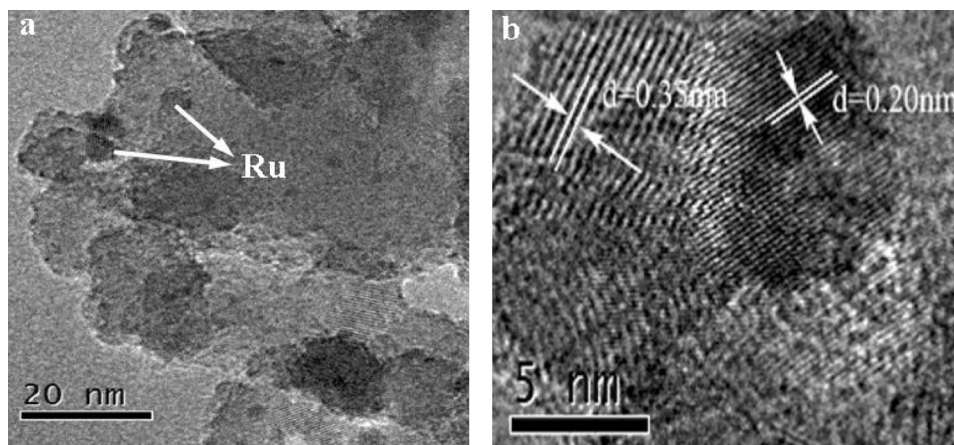


Fig. 1. TEM image (a) and HRTEM image (b) of Ru/TiO₂ sample.

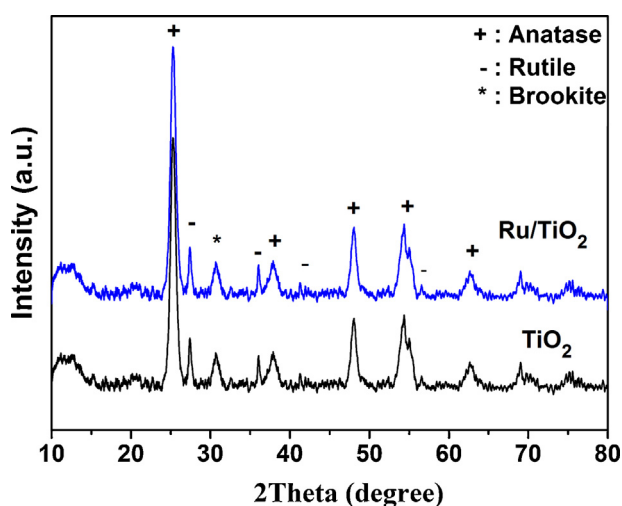


Fig. 2. XRD patterns of TiO₂ and Ru/TiO₂ samples.

Fig. 3 shows the UV–Vis diffused reflectance spectra of TiO₂ and Ru/TiO₂. It is observed that the light absorption capacity of Ru/TiO₂ almost unchanged at wavelength shorter than 400 nm as compared with the bare TiO₂ support. However, a weak absorption peak appears at the visible region (about 450 nm) over Ru/TiO₂,

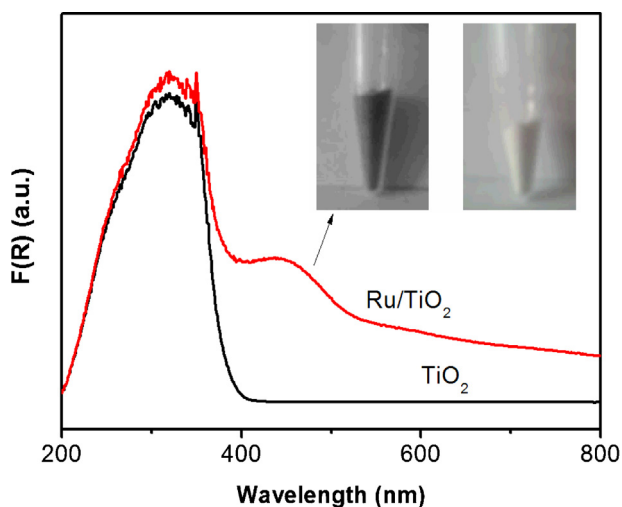


Fig. 3. UV–Vis diffuse reflection spectra of TiO₂ and Ru/TiO₂ samples.

which can be attributed to the located surface plasmon absorption of Ru nanoparticle [24,25].

3.2. Catalytic performances

Fig. 4 shows the conversion of CO as function of reaction temperature over Ru/TiO₂ under UV irradiation or not. It can be seen that the conversion of CO at each temperature (160 °C < T < 210 °C) under UV irradiation is higher than that in dark, resulting in the former presents a sharper temperature dependence of CO conversion below 180 °C. This indicates that UV irradiation can decrease the activation energy for CO methanation over Ru/TiO₂ [26] and then promote the methanation of CO. Moreover, the optimum promotion of UV irradiation is observed at the reaction temperature of 200 °C with a complete conversion of CO to CH₄. However, UV irradiation does not apparently promote the conversion of CO over Ru/TiO₂ at (or below) 160 °C with a low activity in dark. This indicates that the promotion of UV light only occurs on that case of Ru/TiO₂ exhibiting an apparent thermal catalytic activity (an apparent activity in dark) for CO methanation. That is to say, only when the methanation of CO over Ru/TiO₂ proceeds apparently at one temperature in dark, the introduction of UV light can promote the methanation of CO at this temperature to a great extent.

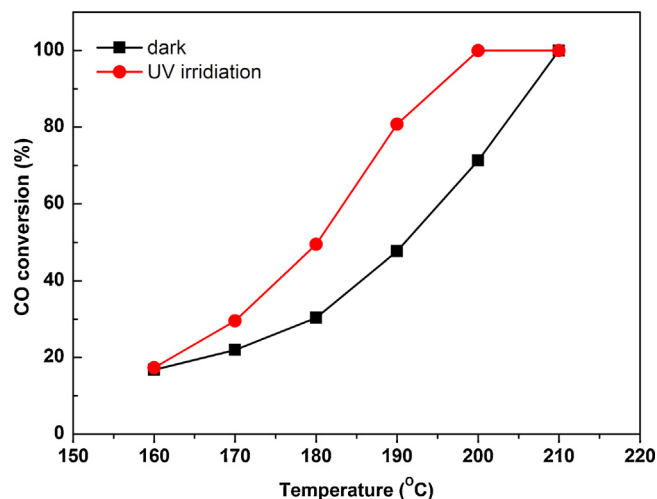


Fig. 4. Conversion of CO at different reaction temperatures over Ru/TiO₂ under UV irradiation or in dark. The CO conversion of each reaction condition was measured after reacting for more 60 min.

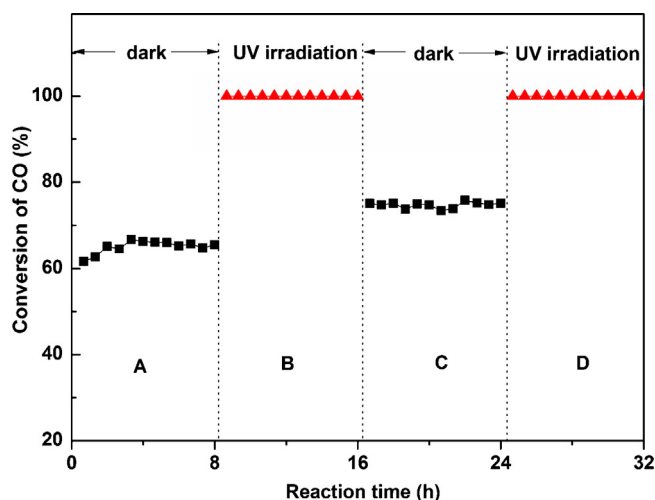


Fig. 5. Conversion of CO as function of reaction time at 200 °C over Ru/TiO₂ under UV irradiation or in dark.

Furthermore, the stability of the promotion of UV light on CO methanation over Ru/TiO₂ was investigated at the reaction temperature of 200 °C. As can be seen in Fig. 5, the conversion of CO in the dark is increased slowly with the increase of reaction time, and kept at about 65.0% after 4 h (process A). With the introduction of UV light (300–420 nm), the conversion of CO is rapidly increased to 100% (process B). Moreover, the conversion of CO drops down to about 72.0% with the removal of UV light (process C), but increased to 100% again with the re-introduction of UV light (process D).

Since the UV light (300–420 nm) can not cause the optical response of Ru nanoparticles (the absorption peak at about 450 nm, seen in Fig. 3), the promoted effect of UV light can be attributed to the optical absorption of TiO₂ support. To demonstrate it, a Al₂O₃ (without optical response at 300–420 nm) supported Ru catalyst (Ru/Al₂O₃) was prepared and then performed for the methanation of CO under UV irradiation. It is found that the introduction of UV light does not promote the conversion of CO over Ru/Al₂O₃ (seen in Fig. 6). This indicates that the promotion of UV light for the methanation of CO over Ru/TiO₂ can be attributed to the band-gap excitation of TiO₂ support. Note that the conversion of CO in the dark over Ru/Al₂O₃ (processes A and C in Fig. 6) is lower than that over Ru/TiO₂ (processes A and C in Fig. 5). This can be attributed to strong interaction between the metal and support

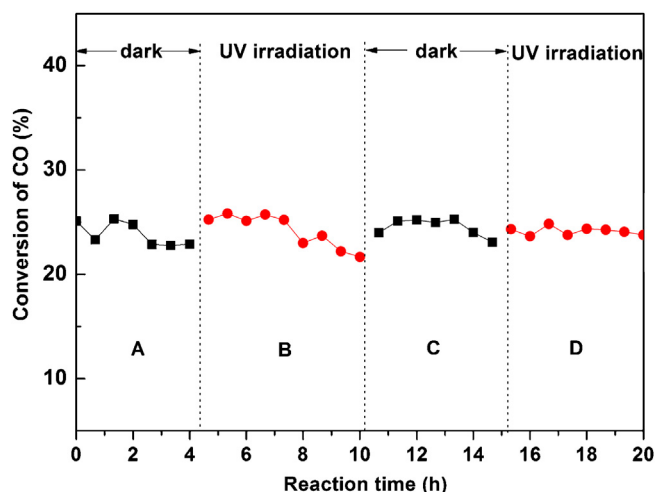


Fig. 6. Conversion of CO as function of reaction time at 200 °C over Ru/Al₂O₃ under UV irradiation or in dark.

(SMSI effect) occurred on Ru/TiO₂ catalyst. In fact, this SMSI effect can be described as the electron transfer from TiO₂ to Ru due to the former having a lower working function than the latter [23]. However, there does not exist the SMSI effect (the electron transfer from Al₂O₃ to Ru) between Al₂O₃ and Ru due to the working function of Al₂O₃ being higher than that of Ru. This will cause a lower electron density of Ru and then a lower catalytic activity than Ru/TiO₂.

In our previous works [19,27], we suggested that a higher surface electron density of Pt and Au would be favorable for the activation of CO species adsorbed at the surface of Pt or Au, and then promote the oxidation of CO. To interpret the promoted effect of UV light for CO methanation over Ru/TiO₂, the surface electron density of Ru and the adsorption of CO at Ru sites under UV irradiation or not was also studied via XPS and FT-IR testing, respectively.

Fig. 7 shows the high-resolution XPS results of Ru/TiO₂ samples under different treatment. Besides the standard peak of C1s of graphite at 284.6 eV, the peak at 285.8 and 288.7 eV can be ascribed to the spectra of C1s of the adsorbed hydrocarbons or carbonates, which were presumably picked up during exposed to the air or produced during the low-temperature drying process. Moreover, the peaks at 279.3–280.7 eV can be ascribed to the spectra of Ru3d_{5/2} [28] (Ru3d_{5/2} spectrum overlapped by C1s spectra at 284.6 eV). The amplified spectra of Ru3d_{5/2} of the three samples are shown in the right part of Fig. 7. As compared to the fresh Ru/TiO₂ (the binding energy at 280.7 eV means that some Ru nanoparticles maybe exist in the state of Ru cations), the Ru/TiO₂ reacted in dark exhibits a lower binding energy of Ru3d_{5/2} (from 280.7 to 279.5 eV), which can be attributed to the electron-donating ability of the dissociated H species over the active site of Ru during the reaction process (Ru species reduced by H₂) [29]. Furthermore, the binding energy of Ru3d_{5/2} of the Ru/TiO₂ reacted under UV irradiation is even lower than that in dark (from 279.5 to 279.3 eV), indicating that UV irradiation can increase the surface electron density of Ru species over Ru/TiO₂. This may be because that the photo-generated electrons in the conduction band of TiO₂ induced by UV irradiation can transfer to the adjacent Ru nanoparticles, resulting in the increase of the surface electron density of Ru sites [23]. Moreover, this electron transfer induced by the band-gap excitation of TiO₂ is somewhat irreversible in the reduced atmosphere (also regarded as a process of Ru species reduced by UV light). Note that the Ru species almost exist in the state of metal Ru over the two reacted Ru/TiO₂ samples.

Further compared the XPS result in Fig. 7 with the activity result in Fig. 5, it can be seen that the conversion of CO is closely concerned with the surface electron density of Ru species. For the fresh Ru/TiO₂ sample with some Ru cations (280.7 eV of Ru3d_{5/2}, Ru species not well-reduced by NaBH₄), although it was pre-treated by H₂ at 300 °C for 2 h before introducing reactant stream, there maybe still exists a tiny of Ru cations over Ru/TiO₂. Thus, the introduced reactant (CO–H₂) maybe further reduce the remained Ru cations (i.e., increasing the surface electron density of Ru) and then promote its activity at the first 4 h during the process A in Fig. 5. With the introduction of UV light, the further increase of surface electron density of Ru species (from 279.5 to 279.3 eV of Ru3d_{5/2}) promote the methanation of CO in process B in Fig. 5. Note that the conversion of CO (72.0%) in process C is higher than that (65.0%) in process A in Fig. 5 (both under no UV irradiation). This maybe because that some accepted electrons of Ru from TiO₂ induced by UV irradiation in process B can remain at Ru surface in the reduced atmosphere in process C. That is to say, the photo-induced electrons transferred from TiO₂ to Ru can not be totally recombined with the photo-induced holes with the removal of UV light, because some of the photo-induced holes can be accepted by the reduced atmosphere, such as CO and H₂. In addition, the activity of Ru/TiO₂ keeps stable during each reaction processes (both in dark and under UV irradiation). This means that the surface electron density of Ru species can maintain during each process (i.e., the electrons no loss).

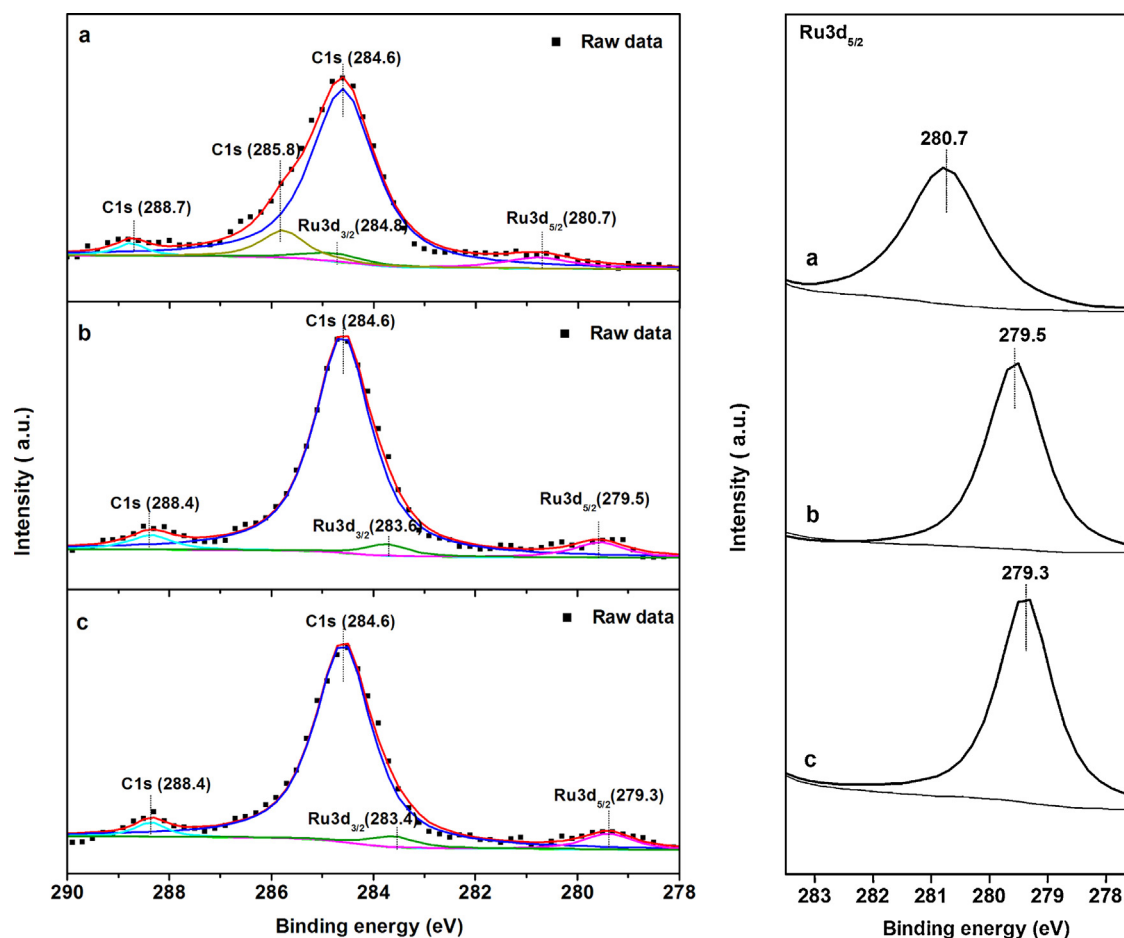


Fig. 7. High-resolution XPS spectra of Ru3d and C1s of Ru/TiO₂ catalysts: (a) fresh catalyst without H₂ pre-treatment at 300 °C; (b) after reaction at 200 °C for 24 h in dark; (c) after reaction at 200 °C for 24 h under UV irradiation.

Moreover, the non-aggregation of Ru species proceeds during the above process (seen in supporting information) can also keep the stability of CO methanation over Ru/TiO₂.

In our previous report [19], it is proposed that this change of surface electron density of Au over Au/TiO₂ can change the adsorption behavior of CO at Au sites and then promote the oxidation of CO. With this viewpoint, the above change of surface electron density of Ru over Ru/TiO₂ induced by UV irradiation maybe also cause the change of adsorption behavior of CO at Ru sites, resulting in the promotion of CO methanation. To demonstrate it, a FT-IR test about the as-prepared Ru/TiO₂ adsorbing CO under UV irradiation or not has been conducted. As shown in Fig. 8, a peak at about 2060 cm⁻¹ is observed after Ru/TiO₂ adsorbing CO in dark (seen in curve b), which can be attributed to the linearly adsorption of CO at Ru sites [30–32]. With the introduction of UV light, the peak of CO adsorbed at Ru sites is shifted to a lower frequency (from 2060 to 2055 cm⁻¹) (seen in curve c). Moreover, the peak intensity (peak height) of CO adsorbed at Ru sites under UV irradiation is about twice as that under dark (curve c vs. curve b).

Based on the XPS result of Ru/TiO₂ in Fig. 7, this above FT-IR result can be explained as follows: During the process of Ru/TiO₂ adsorbing CO under UV irradiation, the photo-generated electrons induced by TiO₂ can transfer to Ru surface, resulting in the increase of surface electron density of Ru sites. This extra electrons of Ru can transfer to the π^* orbital of CO molecule adsorbed at Ru sites ($\{Ru-C=O\}$) according by the principle of $d-\pi^*$ back-donation [22,33], which strengthen the bond of Ru–C but weaken the strength of C–O bond. Thus, more CO with a lower frequency

of the infrared vibrational spectrum is adsorbed at Ru sites under UV irradiation. That is to say, the introduction of UV light during the process of Ru/TiO₂ adsorbing CO does promote the adsorption of CO and its activation at Ru sites.

The above weakened effect of UV light on the C–O bond of CO adsorbed at Ru sites may ultimately promote the formation of CH₄.

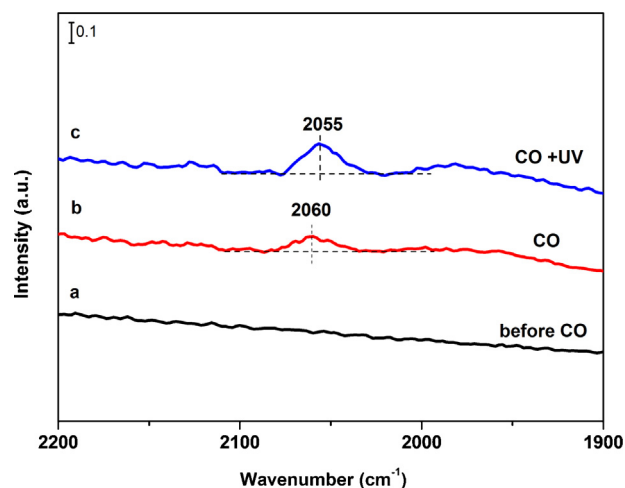


Fig. 8. FT-IR spectra of adsorbing CO over Ru/TiO₂ under different conditions: (a) before adsorbing CO; (b) after adsorbing CO in dark; (c) after adsorbing CO under UV irradiation.

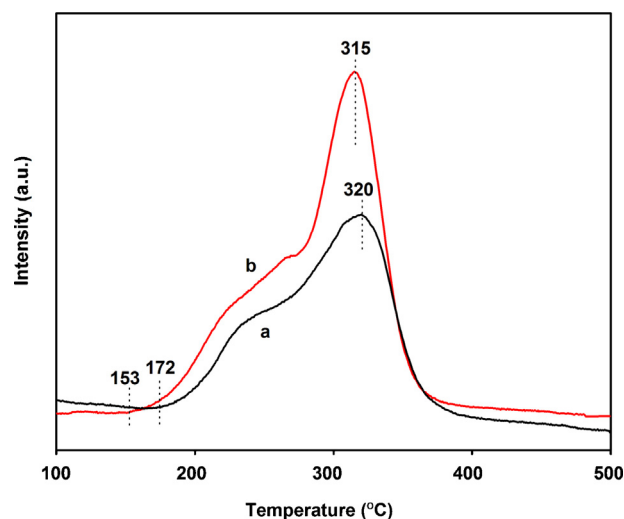


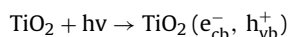
Fig. 9. Mass signals of methane ($m/e = 16$) during the TPSR process over Ru/TiO₂ after adsorbing CO in dark (a) and under UV irradiation (b).

This hypothesis seems to be confirmed by a TPSR testing of Ru/TiO₂ (seen in Fig. 9). As compared to the case of Ru/TiO₂ adsorbing CO in dark, the introduction of UV light during the process of Ru/TiO₂ adsorbing CO can produce a more CH₄ at a lower temperature. Since no UV irradiation is added during the process of introducing H₂ into Ru/TiO₂ accompanied by the increase of temperature, it can be inferred that the promoted effect of UV irradiation on the formation of CH₄ is really attributed to the promotion of CO adsorbed and its activation at Ru sites.

Note that the desorption temperature of CH₄ in Fig. 9 is higher than the reaction temperature of forming CH₄ in Fig. 5. This may be attributed to the different condition of testing TPSR with that of testing catalytic performance, especially the different concentration of CO and H₂ in two cases. On the one hand, the lower content of H₂ during the process of testing TPSR maybe suppresses the methanation of CO, resulting in the increase of temperature of forming CH₄ over Ru/TiO₂. On the other hand, the absence of CO in H₂ stream for TPSR may suppress the desorption of CH₄ at Ru sites.

To further interpret the mechanism of CO methanation over Ru/TiO₂ under UV irradiation, the process of the thermal methanation of CO needs to be known. Although many different mechanism of CO methanation over the supported metal catalysts have been proposed [16,34–38], there is a general agreement that the surface activated carbon (Ru–C), formed by the dissociative adsorption of CO along with the formation of H₂O (CO_{ad} + H_{2ad} → Ru–C + H₂O), would play a crucial role in the thermal methanation of CO on Ru catalyst (XPS results in Fig. 7 also show more carbon species (larger C1s peak) appeared over the two reacted Ru/TiO₂ samples). This surface carbon species will react with the adsorbed hydrogen species to form methane. Combined this viewpoint with the above FT-IR and TPSR results, the extra reaction process of CO methanation over Ru/TiO₂ under UV irradiation can be described as follows.

- (1) Band-gap excitation of the TiO₂ support under UV irradiation resulting in the generation of electron–hole pairs:



- (2) Photo-generated electrons transfer to Ru sites, resulting in the activation of CO adsorbed at Ru sites:

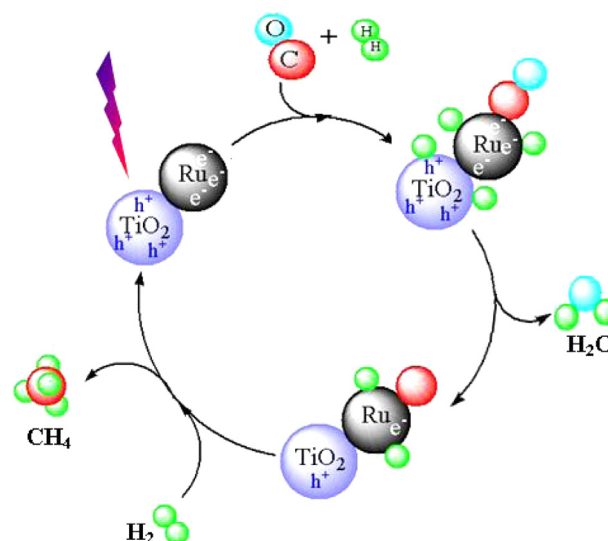
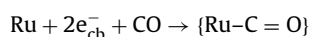
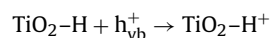
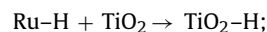
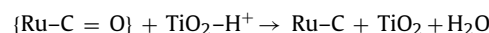


Fig. 10. Schematic of reaction process of CO methanation over Ru/TiO₂ under UV irradiation.

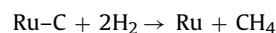
Meanwhile, dissociation adsorption H at Ru sites spillover onto TiO₂ sites to trap with the photo-generated holes [39,40]:



- (3) H⁺ at TiO₂ sites reacting with the activated CO adsorbed at Ru sites to form Ru–C species with the concomitant of H₂O:



- (4) Ru–C species reacting with H₂ to produce CH₄ (producing methane via successive hydrogenation of the surface activated carbons):



During these above processes, the band-gap excitation of TiO₂ under UV irradiation can be acted as an electron donor to offer electrons to Ru sites. It is the photo-excitation of TiO₂ and its electron transfer that cause the subsequent reaction processes. The process schematic of CO methanation over Ru/TiO₂ under UV irradiation can be described in Fig. 10. However, further investigation is needed to look for more direct evidence about the promoted effect of electron transfer on the catalytic reaction.

Note that this promoted effect of UV irradiation on the methanation of CO over Ru/TiO₂ is similar to that on the methanation of CO₂ over Ru–RuOx/TiO₂ reported by Thamphi et al. [41,42]. They also claimed that the promoted effect of UV irradiation can be attributed to the photo-excitation of the support material.

4. Conclusions

UV irradiation can promote the methanation of CO over Ru/TiO₂ above the thermal activation temperature. After testing XPS, FT-IR and TPSR of Ru/TiO₂ under UV irradiation, it is found that UV irradiation can increase the surface electron density of Ru sites, and also promote the adsorption of CO at Ru sites and its activation. It is proposed that the photo-generated electrons induced by the

band-gap excitation (intrinsic excitation) of TiO_2 under UV irradiation can transfer to the adjacent Ru sites to increase the surface electron density of Ru sites. This behavior would further promote the adsorption of CO specie at Ru sites and its activation, resulting in photo-assisted catalytic methanation of CO over Ru/ TiO_2 .

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (nos. 21073037 and 21273037) and the National Basic Research Program of China (973 Program, no. 2014CB239303).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.09.035>.

References

- [1] A.K. Shukla, A.S. Aricò, V. Antonucci, *Renewable & Sustainable Energy Reviews* 5 (2001) 137–155.
- [2] L. Carrette, K.A. Friedrich, U. Stimming, *Fuel Cells* 1 (2001) 5–39.
- [3] A.F. Ghenciu, *Current Opinion Solid State and Materials Science* 6 (2002) 389–399.
- [4] S. Gamburgzev, A.J. Appleby, *Journal of Power Sources* 107 (2002) 5–12.
- [5] G.C. Bond, *Metal-Catalysed Reactions of Hydrocarbons*, first ed., Springer Science+Business Media Inc., New York, USA, 2005.
- [6] M.B.I. Choudhury, S. Ahmed, *Applied Catalysis A: General* 314 (2006) 47–53.
- [7] Q. Liu, L. Liao, Z. Liu, *Chinese Journal of Chemical Engineering* 19 (2011) 434–438.
- [8] L. Shore, R.J. Farrauto, W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), *Handbook of Fuel Cells: Fundamentals Technology and Applications*, 3, John Wiley & Sons Ltd, West Sussex, 2003, p. 211.
- [9] S. Takenaka, K. Kawashima, H. Matsune, M. Kishida, *Applied Catalysis A: General* 321 (2007) 165–174.
- [10] O. Görke, P. Pfeifer, K. Schubert, *Catalysis Today* 110 (2005) 132–139.
- [11] M.S. Batista, E.I. Santiago, E.M. Assaf, E.A. Ticianelli, *Journal of Power Sources* 145 (2005) 50–54.
- [12] M.B.I. Choudhury, S. Ahmed, M.A. Shalabi, T. Inui, *Applied Catalysis A: General* 314 (2006) 47–53.
- [13] Y. Men, G. Kolb, R. Zapf, V. Hessel, H. Löwe, *Catalysis Today* 125 (2007) 81–87.
- [14] M. Krämer, M. Duisberg, K. Stöwe, W.F. Maier, *Journal of Catalysis* 251 (2007) 410–422.
- [15] R.A. Dagle, Y. Wang, G.-G. Xia, J.J. Strohm, J. Holladay, D.R. Palo, *Applied Catalysis A: General* 326 (2007) 213–218.
- [16] Z.G. Zhang, G. Xu, *Catalysis Communications* 8 (2007) 953–956.
- [17] L. Fan, N. Ichikuni, S. Shimazu, U. Takayoshi, *Applied Catalysis A: General* 246 (2003) 87–95.
- [18] H. Hakkinen, U. Landman, *Journal of the American Chemical Society* 123 (2001) 9704–9705.
- [19] Z.X. Ding, H.Y. Yang, J.F. Liu, W.X. Dai, X. Chen, X.X. Wang, X.Z. Fu, *Applied Catalysis B: Environmental* 101 (2011) 326–332.
- [20] W.X. Dai, X.P. Zheng, H.Y. Yang, X. Chen, X.X. Wang, P. Liu, X.Z. Fu, *Journal of Power Sources* 188 (2009) 507–514.
- [21] W.X. Dai, X. Chen, X.X. Wang, P. Liu, D.Z. Li, G.S. Li, X.Z. Fu, *Physical Chemistry Chemical Physics* 10 (2008) 3256–3262.
- [22] H.R. Zheng, H.Y. Yang, R.R. Si, W.X. Dai, X. Chen, X.X. Wang, P. Liu, X.Z. Fu, *Applied Catalysis B: Environmental* 105 (2011) 243–247.
- [23] W.X. Dai, X.X. Wang, P. Liu, Y.M. Xu, G.S. Li, X.Z. Fu, *Journal of Physical Chemistry B* 110 (2006) 13470–13476.
- [24] M.P. Cline, P.W. Barber, *Journal of the Optical Society of America B: Optical Physics* 3 (1986) 15–21.
- [25] Z.Q. Tian, B. Ren, D.Y. Wu, *Journal of Physical Chemistry B* 106 (2002) 9463–9483.
- [26] A.Z. Moshfegh, A. Ignatiev, *Energy* 12 (1987) 277–282.
- [27] J.F. Liu, R.R. Si, H.R. Zheng, Q. Geng, W.X. Dai, X. Chen, X.Z. Fu, *Catalysis Communications* 26 (2012) 136–139.
- [28] J. Chastain, C. Roger King Jr. (Eds.), *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota, USA, 1995.
- [29] C. Mario, L. Foti, C. Ross, K.U. Barclay, Ingold, *Journal of the American Chemical Society* 124 (2002) 12881–12888.
- [30] C. Crisafulli, R. Maggiore, S. Scirè, S. Galvagno, *Journal of the Chemical Society, Faraday Transactions* 90 (1994) 2809–2813.
- [31] G.H. Yokomizo, C. Louis, A.T. Bell, *Journal of Catalysis* 120 (1989) 1–14.
- [32] C. Crisafulli, S. Scirè, R. Maggiore, S. Minicò, S. Galvagno, *Catalysis Letters* 59 (1999) 21–26.
- [33] G. Blyholder, *Journal of Physical Chemistry* 68 (1964) 2772–2777.
- [34] S.I. Fujita, H. Terunuma, M. Nakamura, N. Takezawa, *Industrial and Engineering Chemistry Research* 30 (1991) 1146–1151.
- [35] N.M. Gupta, V.S. Kamble, R.M. Iyer, K.R. Thampi, M. Grätzel, *Journal of Catalysis* 137 (1992) 473–486.
- [36] N.M. Gupta, V.P. Londhe, V.S. Kamble, *Journal of Catalysis* 169 (1997) 423–437.
- [37] S. Eckle, Y. Denkwitz, R.J. Behm, *Journal of Catalysis* 269 (2010) 255–268.
- [38] P. Panagiotopoulou, D.I. Kondarides, X.E. Verykios, *Catalysis Today* 181 (2012) 138–147.
- [39] T. Shishido, H. Hattori, *Applied Catalysis A: General* 146 (1996) 157–164.
- [40] Y. Kohno, H. Hayashi, S. Takenaka, T. Tanaka, S. Yoshida, *Journal of Photochemistry and Photobiology A: Chemistry* 126 (1999) 117–123.
- [41] K.R. Thampi, J. Kiwi, M. Gra, Ètzel, *Nature* 327 (1987) 506–508.
- [42] K.R. Thampi, J. Kiwi, M. Gra Ètzel, *Proceedings of the Ninth International Congress on Catalysis*, vol. 2, 1988, p. 837.